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ELECTROCHEMICAL DEPOSITION OF NICKEL COATINGS FROM ACETATE-CHLORIDE ELECTROLYTE IN PULSE MODE

The process of electrodepositing of nickel from acetate-chloride electrolyte at low temperature in a pulsed mode has been investigated. It is established that application of pulsed electrolysis mode allows to increase the working current density up to 9 A/dm^2. A nanostructured nickel coating with a maximum size of crystallites of 200 nm is obtained. The results show that the use of pulsed electrolysis makes possible to reduce porosity of coating thicknesses up to 20 μm.

Introduction. Pulse and reverse currents are increasingly common in the sphere of electroplating [1]. This is due to wide possibilities to control the structure, properties and quality of obtained coatings, including their appearance and the ability to intensify the processes of deposition compared to conventional electrolysis. Pulse electrolysis allows to receive nanostructured coatings that have properties different from those of conventional coating grain size [2, 3].

The advantage of using a pulsed electrolysis mode is the greatest process flexibility, which is caused by the appearance of a much larger number of independent parameters that control the deposition process (pulses and pauses, cathodic and anodic current density) in comparison with electrolysis without imposing pauses. This enhances the process control and allows to receive coating with desired properties.

Pulse electrolysis is a promising method of coating deposition as in some cases it allows to improve technological process, without modifying the electrolyte composition. In some cases selection ratios of pulses and pauses makes it possible to avoid adding of costly additives. This contributes to simplification of the electrolyte composition, the better management of the process, facilitates the treatment of wastewater, and also offers advantages in terms of reuse of metal salts in the electroplating process [4].

The main disadvantage of electrolytes which are currently often used in industry for the production of nickel coating is increased temperature to 45–55°C. This results in additional energy costs during the coatings deposition, evaporation of the electrolyte, and thus the need for constant adjustments of composition. Besides it is necessary during the technological process to take into account the time for warming the bath to the desired temperature [5].

The most commonly used buffer additive when nickel plating is boric acid, which is a part of many acidic electrolytes. The salts of acetic acid are considered to be more effective buffer additives. In addition, the acetate anions and ammonium ions when reacting with nickel form complex compounds such as $Ni(NH_3)_4^{2+}$, $Ni(NH_3)_6^{2+}$, $Ni(CH_3COO)^+$ [6], which contribute to higher buffer capacity and allow to maintain a constant pH in the cathode region. Complexing in cathode deposition of metals is traditionally used to control both rates of discharge stage and crystallization, and the quality of the cathode deposit. This electrolyte produces nickel coatings at room temperature [7–9].

The aim of this work was to study the process of electrodepositing of nickel from acetate-chloride electrolyte in a pulsed mode at low temperatures.

Main part. As buffer additives in the electrolyte of nickel-plating was used ammonium acetate. The total concentration of Ni^{2+} in the electrolyte is 0.95 mol/dm^3, the concentration of CH_3COO^- 0.36 mol/dm^3 at pH = 4.8. pH of the electrolyte was supporting by pH meter pH-150 with an accuracy of ±0,05. To the desired pH = 4.8 electrolytes were corrected by concentrated acetic acid or NH_3. This allows to receive an acetate buffer mixture $CH_3COOH + CH_3COO^-$. As anode was used a plate of metallurgical nickel H0. The coating quality was adjusted visually.

Buffering capacity of the solutions was determined by potentiometric titration assisted by a universal ion meter with glass indicator electrode. The volume of solutions of nickel salts was 0.05 dm^3. For the titration it was used 5 n. solution of NaOH. The current efficiency of nickel was determined by gravimetric method.

Investigations were carried out in the electrolyte with the composition shown in the table.

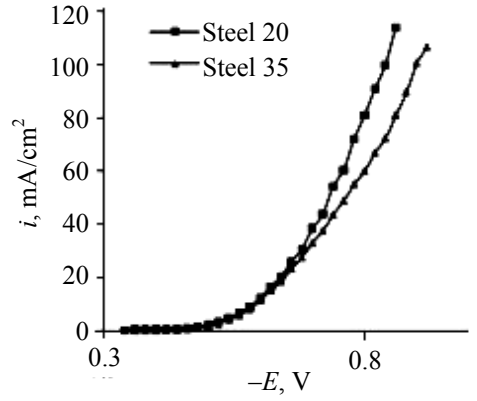
The composition of the studied acetate electrolyte and modes of coating deposition

Parameter	Parameter value			
Composition, g/l: $NiCl_2 \cdot 6H_2O$	226			
CH_3COONH_4	28			
Temperature, °C	20			
pH	4.8			
Current density, A/дм^2	1, 3, 5, 7, 9			
Pulse, s	1			
Pause, s	00.05	00.1	00.2	00.5
Pulse, s	0.1			
Pause, s	00.005	00.01	00.02	00.05

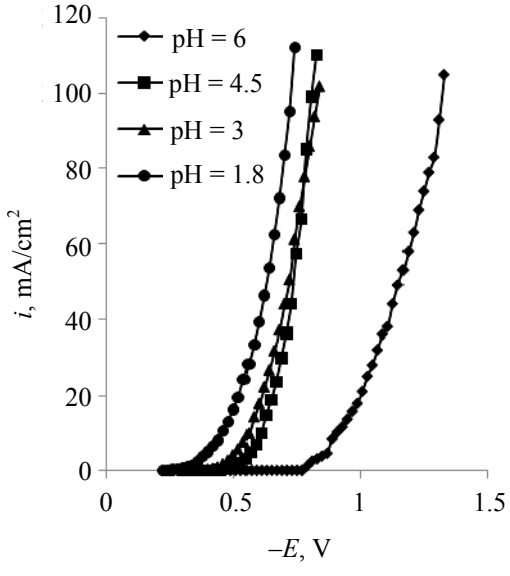
For the formation of step and linear time-varying voltages was used potentiostat PI-50-1.1, as a unit of a programmer PR-8. Automatic registration of the functional dependence of $E(\tau)$ was carried out using the potentiostat IPC Pro as a unit of a PC. The area of the working electrode was 1 cm^2.

The study of electrochemical processes at the border of electrode – electrolyte was carried out in potentiostatic mode. As working electrode were used different types: steel 3, steel 20, and steel 35. The potential of the working electrode was measured in reference to silver-chlorine half-cell and recalculated according to the standard hydrogen scale. The time of establishing of the equilibrium potential was 5 min.

The application of various steel grades as a cathode material has a significant effect on the polarization characteristics of the cathode (Fig. 1, *a*). It was revealed that an increase in the carbon content of the steel shifts polarization curve in the negative direction at potentials more electronegative than –0.7 V.



a



b

Fig. 1. The influence of the substrate material (*a*) and different pH (cathode – steel 3) (*b*) on the polarization characteristics of the cathode

In Fig. 1, *b* it is shown the effect of pH value on the cathodic polarization. The obtained data reflect the known tendency to decrease the polarization of the cathode with the acidification of the electrolyte, as with a reduction of pH value together with nickel at the cathode more hydrogen is produced. This, in turn, increases the risk of pitting. The acidity of the electrolyte strongly affects the mechanical properties and structure of electrodeposited nickel coatings.

In Fig. 2 it is shown dependence of the current efficiency on the current density at different pause time.

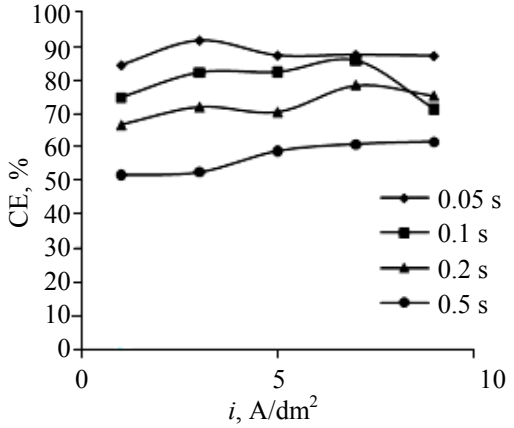
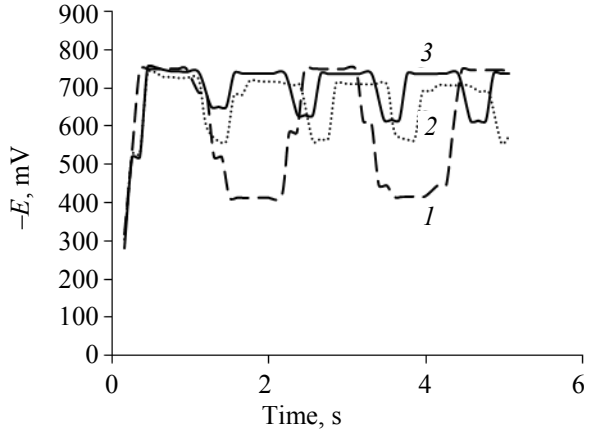


Fig. 2. The dependence of the current density on the current efficiency in the pulse of 1 s at intervals 0.05, 0.1, 0.2, 0.5 s

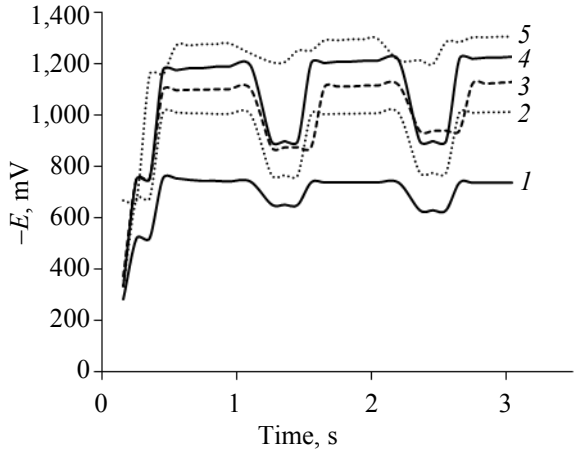
Efficiency increases with the decrease of time of pause and constitute in pulse modes up to 50–95%. The application of pulses with duration 1 and 0.1 s resulted in improved appearance of the coating, in contrast to the coatings obtained in stationary mode: depositions of nickel were semi-glittering with a rare pitting. It should be noted that the pulsed electrolysis increases the permissible current density. In stationary mode current density does not exceed 6 A/dm^2, and in pulsed – 9 A/dm^2.

The authors of [4] explain the difficulty of deposition of nickel in the mode without input of pulses at high current densities by formation of the adsorption hydroxyl compounds of nickel on the electrode surface. When pulsed electrolysis the partial release rates of the metal and hydrogen is redistributed in current pulse in favor of the metal. It results in less cathode pH shift towards higher values, and, consequently, the formation of the basic compounds of nickel on the electrode surface is inhibited. The amount of nickel containing components is decreased by discharge. Filling of nickel components in the cathode layer is on account of diffusion during the current pause. The concentration of nickel ions approaches to the concentration in the volume of the electrolyte.

Fig. 3 shows the dependence of potential in time. According to this figure it is obvious that the potential of the electrode during the pause does not relax to its original no-current value, and stays in the spectrum of rather negative values. This may be due to the existence of nickel ions in the cathode layer in the form of various complexes in the first place – acetate.



a



b

Fig. 3. Chronopotentiograms:
a – pulse 1 s, i = 1 A/dm^2 and pause:
1 – 0.5 s; *2* – 0.1 s; *3* – 0.2 s;
b – at current densities of: *1* – 1 A/dm^2;
2 – 3 A/dm^2; *3* – 5 A/dm^2; *4* – 7 A/dm^2;
5 – 9 A/dm^2 (cathode – steel 3)

The study of buffer properties showed that electrolytes of nickel plating containing salt CH_3COONH_4, have a significantly higher buffering capacity than Watts electrolyte that allows to receive coatings by larger current densities. At the same time the maximum buffer capacity ranges from 3.5 to 5.0 units of pH. A wide range of manifestations of the buffer properties of the investigated electrolyte allows the electrolyte to work in a wider range of current density and, consequently, to obtain coatings with high current efficiency.

Determination of the throwing power of the electrolyte was performed in accordance with GOST 9.309-86 in Mohler's cell. Throwing power of the current and the metal in the range of current densities of 1–5 A/dm^2 is 10–22% and 10–19% respectively.

Nickel coating adhesion was studied by the method of bending, according to GOST 9.302-88. In the investigated electrolyte coating passed the test with thickness of 20 and 40 μm. At 60 μm flaking was observed.

In Fig. 4 there is represented a photomicrograph of a nickel coating produced by pulsed electrolysis. In this case, it is clear that the use of non-stationary mode allowed to get finely crystalline coating with maximum crystallite size of 200 nm.

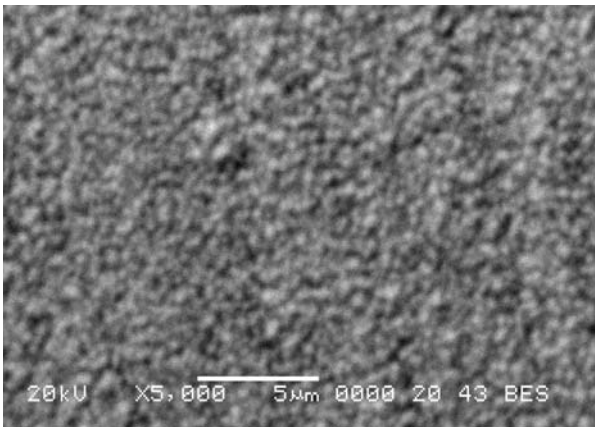


Fig. 4. Photomicrograph
of a nickel coating obtained by i = 9 A/dm^2,
by pulse 1 s, by pause 0.5 s

Fig. 5 shows the dependence of the current efficiency on the logarithm of the pause duration.

The increases of pause time bring about reducing of the efficiency according to the current. It has been found that an increase in the pause time from 0.2 to 0.5 s with a momentum of 1 s, and from 0.02 to 0.05 s with a momentum of 0.1 s results in a decrease of the current efficiency by 10–20%.

An important characteristic of any coating is its porosity. This parameter is defined by nature of the original surface as well as by conditions for obtaining coatings.

Fig. 6 presents comparative data of nickel coating porosity obtained in a stationary (curve *1*) and pulse (curve *2*) modes of electrolysis.

As Fig. 6, under conditions of a pulsed electrolysis at coating thickness less than 20 μm, it is observed a decrease of porosity up to 30% compared to conventional electrolysis.

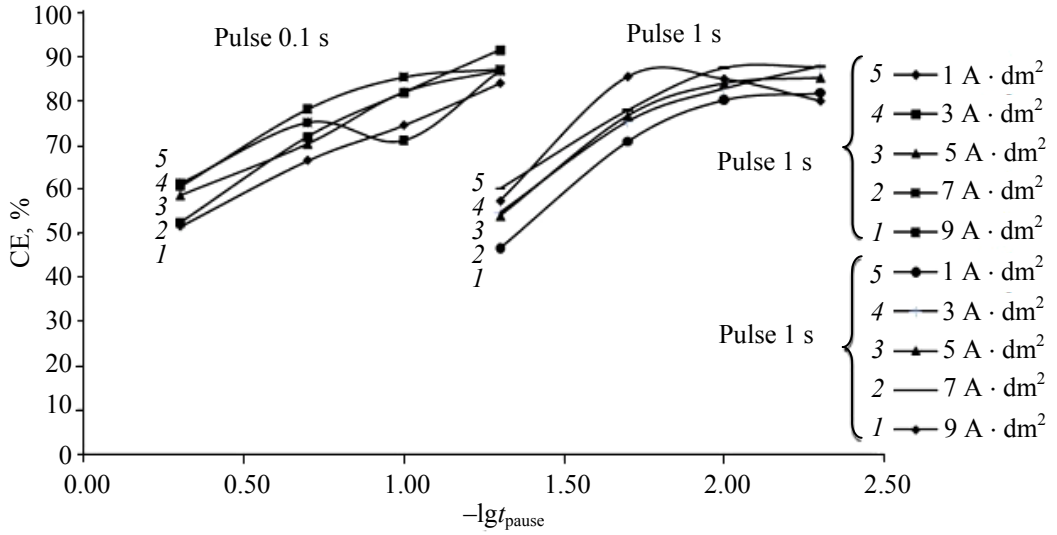


Fig. 5. The dependence of the current efficiency on the logarithm of the pause duration

From the thickness of 20 μm electrolysis mode has almost no effect on the porosity of the coating.

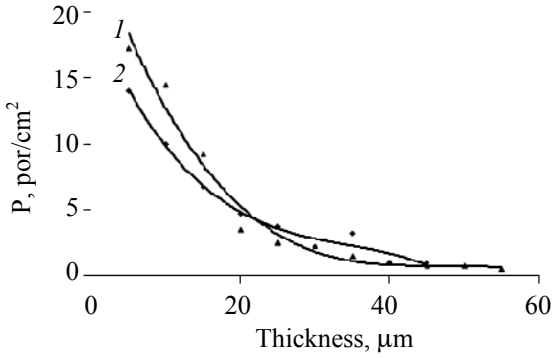


Fig. 6. The dependence of the porosity of the coating at the thickness of the stationary (curve *1*) and pulse (curve *2*) electrolysis

Conclusion. It has been found that the use of pulsed electrolysis mode allows to increase working current density up to 9 A/dm^2, to get nanostructured nickel coating with maximum crystallite size of 200 nm. These data show that the use of pulsed electrolysis reduces porosity at thicknesses up to 20 μm. For receiving of high quality nickel coatings with pulsed electrolysis the following most optimal parameters are suggested in the investigated electrolyte: pulse – 1 s, pause – 0.1, 0.05 s or pulse – 0.1 s, pause – 0.01, 0.005 s at current density 7 A/dm^2.

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